MESOPOROUS MCM-48 SYNTHESIZED FROM RICE HUSK ASH SILICA: PHYSICOCHEMICAL PROPERTIES AND ITS CATALYTIC ACTIVITY IN ACYLATION REACTION

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For the Lord Almighty,

my beloved family

and

specially for Yang Eik Hien

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PREFACE

This thesis is the result of my work carried out in the Department of Chemistry, Universiti Teknologi Malaysia between Jun 2002 to September 2004 under supervision of Assoc. Prof. Dr. Salasiah Endud. Part of my work described in this thesis has been reported in the following publications:

1. Lau, C.G. and Endud, S. (2002). "Sintesis Bahan Mesoliang MCM-48 Menggunakan Campuran Templat Surfaktan Kationik dan Neutral." *Proceedings of the Fifth UKM-ITB Joint Seminar on Chemistry.* Bandar Hilir, Melaka. 16-17 July. 425-432.

2. Lim, K.W., Lau, C.G. and Endud, S. (2002). "High Surface Area Catalysts for Alkylation and Oxidation Reactions". Poster presentation at the *15th Simposium Kimia Analisis Kebangsaan (SKAM-15)*. Universiti Sains Malaysia, Minden, Pulau Pinang. 10-12 September. P 90.

3. Lau, C.G. and Endud, S. (2003). "Optimization of Synthesis of Mesoporous Materials from Carbonaceous Rice Husk Ash". Report for Post-Graduate Study 1st Assessment. Pusat Pengajian Siswazah, Universiti Teknologi Malaysia.

4. Lau, C.G. and Endud, S. (2003). "Synthesis of Mesoporous Materials from Carbonaceous Rice Husk Ash (RHA) and Its Application As Catalyst In Friedel-Crafts Reaction" *Annual Meeting of Zeolite and Porous Materials Group*. A Farmosa, Melaka.

5. Lau, C.G. and Endud, S. (2003). "Hydrothermal Stability of MCM-48 Mesoporous Molecular Sieves: Effect of Aluminium Content". *Proceedings of Annual Fundamental Science Studies*. Johor Bahru, Johor. 20-21 May. 115-120.

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7. Nur, H., Lau, C.G., Endud, S. and Hamdan, H. (2004). "Quantitative Measurement of A Mixture of Mesophases Cubic MCM-48 and Hexagonal MCM-41 by ^{13}C CP/MAS NMR" *Materials Letters*. **58**. 1971-1974.

8. Lau, C.G., Nur, H. and Endud, S. (2004). "Preparation of MCM-48 with A Bimodal Pore Size Structure by Post-Synthesis Alumination". Oral presentation at the *Regional Symposium on Membrane Science & Technology 2004*. Johor Bahru, Johor. 21-25 April.

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10. Lau, C. G., Nur, H. and Endud S. (2005). "Bimodal Pore Size Mesoporous MCM-48 Materials Prepared by Post-Synthesis Alumination". *J. Phys. Sci.* (*accepted*).

ABSTRACT

The cubic structural mesoporous molecular sieves Si-MCM-48 has been successfully controlled by optimizing the gel compositions via a mixed surfactant templating route using cationic cetyltrimethylammonium bromide (CTABr) and neutral Triton X-100 (TX-100) surfactants. Rice husk ash, an agricultural waste obtained from an open burning site with high silica content (93 % SiO_2) has been utilized as active silica reagent in the synthesis process. The Si-MCM-48 mesoporous materials were structurally characterized by X-Ray Powder Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). The results show that the crystallinity and phases of the products depend on the compositions of Na_2O, surfactants, H_2O and pH values. Moreover, ^{13}C CP/MAS NMR technique had been developed to quantify a mixture of cubic MCM-48 and hexagonal MCM-41 mesophases by means of interpretation of their surfactant organization, which cannot be determined by XRD technique. In order to generate active sites for catalytic applications, alumino-mesoporous materials Al-MCM-48 were prepared by post-synthesis alumination of mesoporous Si-MCM-48 and post-synthesis alumination of Si-MCM-48 mesophase using sodium aluminate as the aluminium reagent. The aluminated MCM-48 materials were characterized using XRD, ^{27}Al MAS NMR, FTIR and nitrogen adsorption-desorption measurements. The results reveal that unimodal Al-MCM-48, which possesses narrow pore size distribution around 26Å, had been synthesized from post-synthesis alumination of mesoporous Si-MCM-48. Whereas, bimodal Al-MCM-48, which possesses dual narrow pore size distributions around 26 Å and 38 Å had been generated by post-synthesis alumination of uncalcined Si-MCM-48 mesophase. ^{27}Al MAS NMR results depict that aluminium had been tetrahedrally incorporated into the framework structure of MCM-48. The nature and the concentration of acid sites of Al-MCM-48 materials have been monitored by IR spectroscopy using pyridine as the probe molecule and temperature-programmed desorption of ammonia (TPDA). Acidity studies on the samples demonstrated that the acidity strength of samples prepared via post-synthesis alumination of mesoporous Si-MCM-48 is greater than samples prepared via post-synthesis alumination of Si-MCM-48 mesophase. Aluminated MCM-48 materials have been employed in the acylation of bulky aromatic compound, 2-methoxynaphthalene with acetic chloride to produce 2-acetyl-6-methoxynaphthalene, which is intermediate for preparing naproxen, a non-steroidal anti inflammation drug. Catalytic activities have been investigated in solvents with different polarity and the results illustrate that the conversion and selectivities of products rely on the polarity of solvent. The conversion of the 2-methoxynaphthalene can be as high as 42 % with 86 % selectivities towards the desired 2-acetyl-6-methoxynaphthalene in polar solvent, nitrobenzene. Whereas, the conversion of the 2-methoxynaphthalene is 30 % with 56 % selectivity of 2-acetyl-6-methoxynaphthalene in non-polar solvent, cyclohexane.

ABSTRAK

Penapis molekul mesoliang Si-MCM-48 yang berbentuk kiub telah berjaya disintesis dengan mengoptimumkan komposisi gel melalui kaedah campuran surfaktan kationik setiltrimetilammonium bromida (CTABr) dan surfaktan neutral Triton X-100 (TX-100). Abu sekam padi yang mempunyai kandungan silika yang tinggi (93 % SiO_2), di mana ia diambil daripada kawasan pembakaran terbuka telah digunakan sebagai sumber silika yang aktif dalam proses sintesis ini. Struktur penapis molekul mesoliang Si-MCM-48 ini dicirikan dengan kaedah pembelauan sinar-X (XRD) dan spektroskopi inframerah transformasi Fourier (FTIR). Keputusan menunjukkan darjah kehabluran dan ketulenan fasa bahan mesoliang adalah bergantung kepada komposisi Na_2O, surfaktan, H_2O dan nilai pH. Di samping itu, teknik ^{13}C CP/PSA RMN telah digunakan untuk mengkaji ketulenan fasa campuran MCM-48 yang berfasa kiub dan MCM-41 yang berfasa heksagon secara kuantitatif, di mana ia tidak dapat dilakukan dengan menggunakan kaedah XRD. Aluminium MCM-48 (Al-MCM-48) telah disintesis dengan menggunakan dua kaedah pasca-sintesis untuk menghasilkan tapak aktif pemangkinan, iaitu, penyelitan aluminium ke dalam bingkaian Si-MCM-48 dan penyelitan aluminium ke dalam fasa meso Si-MCM-48 dengan menggunakan natrium aluminat sebagai sumber aluminium. Sampel Al-MCM-48 dicirikan dengan kaedah XRD, ^{27}Al PSA RMN, FTIR dan penjerapan dan nyahjerapan nitrogen. Analisis penjerapan nitrogen menunjukkan liang Al-MCM-48 yang bersebar secara seragam dengan purata liang disekitar taburan 26 Å telah dihasilkan dengan menggunakan kaedah penyelitan aluminium ke dalam bingkaian bahan mesoliang Si-MCM-48. Di samping itu, Al-MCM-48 yang memiliki taburan dua jenis mesoliang yang tertabur di antara 26 Å dan 38 Å telah dihasilkan melalui kaedah penyelitan aluminium ke dalam fasa meso Si-MCM-48 tanpa kalsin. Keputusan ^{27}Al PSA RMN menunjukkan aluminium bingkaian berkordinatan tetrahedral telah dihasilkan melalui kedua-dua kaedah tersebut. Jenis dan kepekatan tapak asid yang terdapat pada permukaan Al-MCM-48 telah ditentukan dengan menggunakan kaedah spektroskopi inframerah menggunakan piridina sebagai molekul prob dan kaedah nyahjerapan ammonia pada suhu terkawal (TPDA). Hasil kajian keasidan menunjukkan sampel yang disediakan melalui penyelitan aluminium ke dalam bingkaian bahan mesoliang Si-MCM-48 adalah lebih kuat daripada sampel yang disediakan melalui penyelitan aluminium ke dalam fasa meso Si-MCM-48 tanpa kalsin. Potensi bahan Al-MCM-48 sebagai mangkin Friedel-Crafts telah diuji dengan menggunakan tindak balas pengasilan sebatian 2-metoksinaftalena dengan asetil klorida untuk menghasilkan 2-asetil-6-metoksinaftalena, bahantara untuk menyediakan *naproxen*, ubat anti-keradangan yang non-steroid. Kajian aktiviti pemangkinan dengan menggunakan pelarut yang berlainan kepolaran menunjukkan peratus pertukaran dan kepilihan produk adalah bergantung kepada kepolaran pelarut. Peratus pertukaran 2-metoksinaftalena boleh mencapai setinggi 42 % dengan 86 % kepilihan kepada 2-asetil-6-metoksinaftalena di dalam pelarut polar (nitrobenzena). Di samping itu, peratus pertukaran 2-metoksinaftalena hanya sebanyak 30 % dengan 56 % kepilihan kepada 2-asetil-6-metoksinaftalena di dalam pelarut yang tidak polar (sikloheksana).

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LIST OF SYMBOLS

RHA	rice husk ash
LOI	loss of ignition
L	litre
mL	millilitre
^{o}C	Celsius
K	Kelvin
g	gram
min	minute
h	hour
MCM	Mobile Composition Materia1
M	molar
Si/Al	silicon-to-aluminium ratio
Si-MCM-48	purely siliceous MCM-48
Al-MCM-48	aluminosilicate MCM-48
XRD	X-Ray diffraction
FTIR	Fourier Transform Infrared
^{27}Al MAS NMR	^{27}Al magic-angle-spinning nuclear-magnetic-resonance
^{13}C CP/MAS NMR	^{13}C cross-polarization magic-angle-spinning nuclear-magnetic-resonance
TPD	temperature-programmed desorption
FESEM	field emission scanning electron microscopy
d	inter-planar spacing
Cu-K_α	X-ray diffraction from copper K_α energy levels
λ	wavelength
kV	kilovolt
mA	milliampere
2θ	Braggs angle

KBr	kalium bromide
TMS	tetramethylsilane
s	second
Hz	Hertz
CaF_2	calcium fluoride
I.D.	internal diameter
GC	gas chromatrography
GC-MS	gas chromatrograpy-mass spectrometry
FID	flame ionization detector
IUPAC	International Union of Pure and Applied Chemistry
AlO_4	aluminate, framework aluminium in zeolite
SiO_4	siliceous; framework silicon in zeolite
TEM	transmission electron microscopy
LCT	liquid crystal templating
g	surfactant packing parameter
BET	Brunauer, Emmett and Teller
Si-OH	silanol group
EFAL	extra framework aluminium
a_o	unit cell parameter
N_2	nitrogen
P/P_o	relative pressure; obtained by forming the ratio of the equilibrium pressure and the vapor pressure P_o of the adsorbate at the temperature where the isotherm is measured.
PSD	pore size distribution
BJH	Barrett, Joyner and Halenda
α_s	alfa-S
R_t	retention time
TON	turnover number
ms	millisecond

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CHAPTER 1

INTRODUCTION

1.1 Green Chemistry for Sustainable Development

In the 21st century, building a sustainable future has been the greatest challenge of the global society. The development of science and technology has become the crucial role in order to fulfilling current need and to preserve a well living environment for the future generations. Therefore, the public, legislative, and environmentalists are urging the development of cleaner technologies to serve mankind. Hence, it has stimulated the exciting opportunities for catalysis and catalytic processes.

Catalyst is a substance, which accelerates the rate of a chemical reaction whilst it may be recovered chemically unchanged at the end of the reaction [1]. The presence of the catalyst is essential for (i) obtaining new structures, (ii) increasing the productivity, (iii) decreasing the raw materials and energy consumption, (iv) minimizing the waste production and getting a better environment [2].

Catalysis is a privileged way to a clean and powerful chemistry. Today, catalysts play a vital role in the chemicals industry, with a total contribution of *ca.* 20% of the world GNP in the 20th century [3]. In addition, 80% of the industrial reactions use catalysts. The British agency Frost and Sullivan, which published a study in 1998 [4] evaluated the catalysts European market to $ 3.7 billions turnover in 1998. With about 4% growth per year, it should increase to $ 5 billions in 2005.

1.2 Heterogeneous Catalysts

Catalysts can be classified into two categories, homogenous and heterogeneous. Homogenous catalyst is the catalyst, which presents in the same phase as the reagents. Sulfuric acid has been widely used as homogenous catalyst in the alkylations or isomerizations of hydrocarbon [5]. Whereas, catalysts are heterogeneous if they are present in a different phase from the reactants. One of the prominent heterogeneous catalysts is zeolites which are extensively employed in petroleum refinery processes [6].

Heterogeneous catalysis is the backbone of the modern chemical industry, because of the necessity to achieve environmental benign processes in the industry. In addition, heterogeneous catalysts offer numerous potential advantages over homogenous catalysts, such as easier working up procedures, easy catalyst separation from the reaction mixture, reduction of environmental pollutant, avoidance of salt formation and waste disposals [7].

Since 1960s, zeolites catalysts have conquered the petroleum refining and petrochemical industries. This is due to the zeolites that have excellent thermal and chemical stability. Moreover, zeolites provide great acid strength, which are comparable to homogeneous acid catalysts [7]. The most important of these processes are hydrocracking of heavy petroleum distillates, octane number enhancement of light gasoline by isomerization, the isomerization of xylenes (to produce *para*-xylene, the precursor chemical for terephthalic acid), and etc [6]. However, the utilization of zeolites in the areas of specialty and fine chemicals synthesis is still limited, even though their potential is considered to be very high in this area as well. The small pore opening of zeolites, in the range of *ca.* 0.2-1 nm, is a major restriction for it to utilize in organic reactions [6]. The reactants with sizes exceeding the dimensions of the pore are not able to process via zeolites. Therefore, numerous attempts have been devoted to increasing the pore size of crystalline molecular sieves [8].

In 1992, a novel family of ordered silicate mesoporous molecular sieves, designated as M41S has been discovered by researchers at Mobil R & D Corporation

[9]. The most important member among these materials is MCM-41 and MCM-48, which possesses hexagonal and cubic symmetry, respectively. The uniqueness of M41S mesoporous materials are the pore size are uniform and tunable in the range between 1.6-10 nm. Furthermore, these mesoporous materials also possess high thermal stability and have extremely high surface areas. This innovative discovery has greatly expanded the area of microporous molecular sieves (zeolites) into the mesopore range and has created new opportunities beyond catalysis. The ordered mesoporous materials have been found as promising materials in optics and electronics, as nano size template, and as adsorbents for heavy metals [10]. The rapid growing of publications in mesoporous materials since 1990 is shown in Figure 1.1 [10].

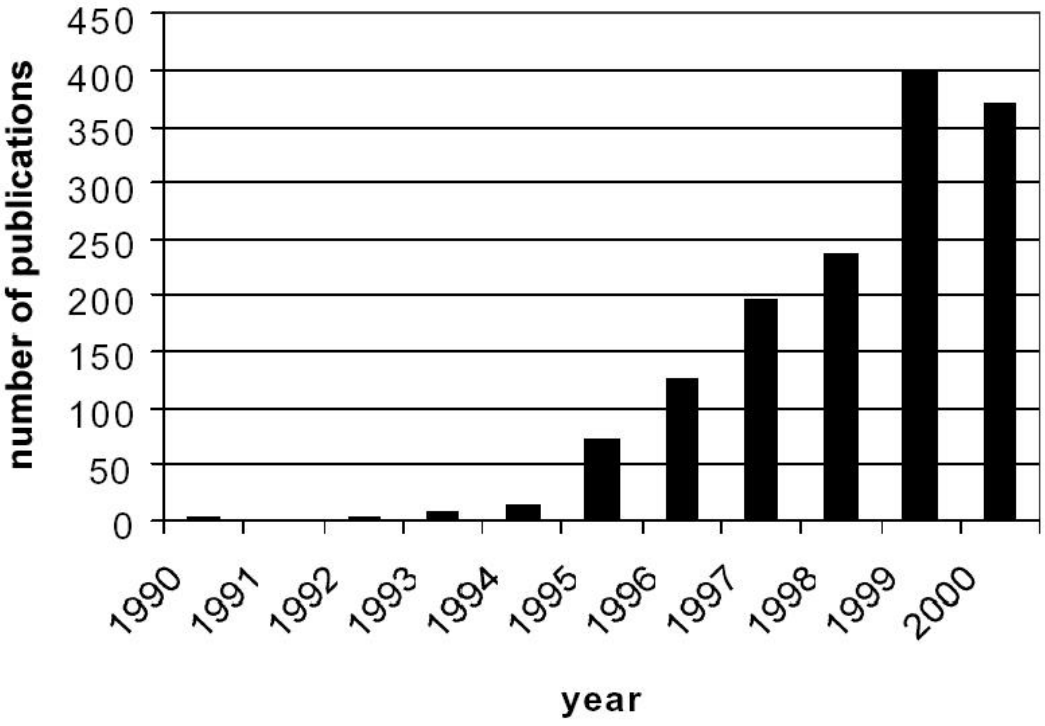

Figure 1.1 Development of publications on ordered mesoporous materials since 1990 [10].

1.3 Research Background and Problem Statement

Malaysia has been found as one of the major rice production country, whereby 425,080 hectares (3.21 % of the total land in peninsular Malayisia) of the land have been used for paddy plantation [11]. Therefore, it generates abundance of waste namely rice husk, a thin but abrasive skin in nature covering the edible rice kernel. It has been reported that Malaysia produces a *ca.* 18 million tons of paddy in which about one fifth of it is the husk [12]. This means that the annual production of rice leaves behind about 3.6 million tons of husk as waste product, usually disposed by combustion. Unfortunately, the 20 % of the rice husk ash (RHA) residues left after the combustion constitute environmental problems due to severe air and water pollution problems. However, RHA can be considered as a potential feature of the rice husk, which the RHA residues can be employed as raw materials in a variety of applications.

Previous research had shown that the rice husk ash containing 96-99% SiO_2 can exist either in amorphous phase or in crystalline phases such as, α-cristobalite and tridymite [13-14]. In fact, the amorphous silica is the most active silica precursor in the synthesis of zeolites. Hence, the large amount of silica freely obtained from this source provides abundant and cheap alternatives of silica for many industrial uses. From the previous report, MCM-41 has been successfully synthesized by using the silica extracted from RHA [15]. However, no report has been found on the synthesis of MCM-48 directly from RHA, since the synthesis of MCM-48 mesoporous materials seems to be more challenging than the synthesis of MCM-41. By using rice husk ash as the silica source in the synthesis of MCM-48, the production costs can be reduced subsequently besides helping to overcome environmental pollution. Indeed, it should be noticed that RHA is considered slightly impure silica. The content of silica and all impurities in RHA vary depending on the variety, climate and geographic location [16]. Therefore, in order to transform the RHA to valuable mesoporous materials, modification and optimization of the synthesis condition should be carried out.

The three-dimensional cubic porous system of MCM-48 mesoporous materials has more advantageous than one-dimensional hexagonal porous system.

However, it is particularly difficult to synthesize MCM-48 mesoporous materials, since cubic MCM-48 mesophase are obtained as an intermediate between the transformation from a hexagonal or disordered mesophase to a more stable lamellar mesophase [17]. Hence, instead of pure phase, the mixtures of different phases are frequently obtained during the synthesis. It is a great challenge to characterize the mesoporous materials, since the XRD is not capable to distinguish the phases in the state of mixtures of different ordered mesophases.

Friedel–Crafts acylation of aromatic compounds is one of the prominent processess in the synthesis of aromatic ketones that has been widely used as an intermediate to obtain fine, specialty and pharmaceutical chemicals. However, the majority of these manufacturing processes still rely on homogeneous reagents and catalysts. Many of these processes are developed simply to maximize product yield, disregarding the environmental impact of inorganic waste and toxic byproducts formed during the reaction. Among the Lewis acid catalysts, anhydrous aluminium chloride was the most widely employed reagent to trigger the Friedel-Crafts reaction in the liquid phase in the laboratory as well as in the industry. However, the use of standard Lewis acid catalyst is faced with several problems, such as non-regenerable, requires further treatment after reaction, produces large amounts of hazardous corrosive waste, catalyzes undesirable reaction, and also uses more than the stoichiometric amount. Therefore, the demand for less pollutant and more effective chemical processes has become the current concern. Zeolites have been found to be less useful in these chemicals processes due to the limitation of its pore opening for bulky organic molecules. Conversely, the emergence of mesoporous materials has breakthrough the restriction of zeolites, since the larger pore size of these materials allows bulky organic molecules to diffuse through the pores to reach the active sites. Moreover, utilization of mesoporous materials such as MCM-48 in the production of fine chemicals is still being studied and developed but is yet to be available commercially.

1.4 Research Objectives

The objectives of this research are:

(1) to establish and optimize a new synthetic mesoporous Si-MCM-48 molecular sieves by using rice husk ash as silica source.

(2) to develop a novel characterization technique for measurement of mesophases composition.

(3) to synthesis and tailor the unimodal and bimodal of Al-MCM-48 via post synthesis route.

(4) to characterize the physicochemical properties of Al-MCM-48.

(5) to investigate the catalytic properties of the Al-MCM-48 in the Friedel-Crafts acylation of 2-methoxynaphthalene with acetyl chloride.

1.5 Scope of the Study

In this research, syntheses of purely siliceous mesoporous Si-MCM-48 molecular sieves via mixed cationic-neutral templating route have been optimized by means of varying the initial condition of original gel compositions proposed by Ryoo *et al.* [17], such as pH value, Na_2O/ SiO_2, surfactant/SiO_2, and H_2O/SiO_2. Cetyltrimethylammonium bromide (CTABr) has been used as cationic surfactant, whereas Triton X-100 (TX-100) as neutral surfactants. Rice husk ash (RHA) which were obtained from open burning site will be used as silica source. Moreover, a novel approach for quantification of mesophase purity by using ^{13}C CP/MAS NMR has been developed in order to verify the mesophases compositions from hexagonal MCM-41 to cubic MCM-48.

Modification of MCM-48 is devoted by introducing the aluminium into the Si-MCM-48 by two post synthesis approaches. Both mesoporous and mesophase of Si-MCM-48 will be employed as parent materials in post-synthesis alumination. Acidity of the samples are investigated by using temperature-programmed desorption (TPD) of ammonia and pyridine adsorption methods.

Appropriate techniques are utilized to characterize the physicochemical properties of the mesoporous materials which include powder X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), nitrogen adsorption-desorption measurement, ^{27}Al magic angle spinning nuclear magnetic resonance spectroscopy (^{27}Al MAS NMR), and field emission scanning electron microscopy (FESEM).

Finally, the mesoporous catalysts will be tested as potential catalysts in laboratory scale. Investigation of its catalytic activity will be conducted using Friedel-Crafts acylation of bulky aromatic compound, 2-methoxynaphthalene with acetyl chloride. Solvents with various polarities such as cyclohexane, dichloroethane, and nitrobenzene will be used in this study. The research design is schematically illustrated in Figure 1.2.

1.6 Outline of the Thesis

This thesis illustrates the information concerning the synthesis, characterization and the potential catalytic application of mesoporous MCM-48 molecular sieves. Chapter 1 elucidates the research background and the strategies to respond the current issue. Chapter 2 describes the experimental methodology. Whereas, Chapter 3 covers the chemistry and fundamental aspects of mesoporous MCM-48 molecular sieves. The results of the optimization of synthesis of mesoporous MCM-48 molecular sieves are also present in this chapter. Chapter 4 explains the novel technique for quantification of mesophases compositions by using ^{13}C CP/MAS NMR. Chapter 5 contains the studies in tailoring the unimodal and bimodal of Al-MCM-48 by using different post-synthesis alumination approaches. Chapter 6 reveals the discussion of the acidity studies of Al-MCM-48 by using NH_3-TPD and pyridine adsorption. In addition, the catalytic activity of Al-MCM-48 catalysts, which is tested by Friedel-Crafts acylation is presented in this chapter too. Finally, Chapter 7 summarizes the results obtained with recommendation for future work.

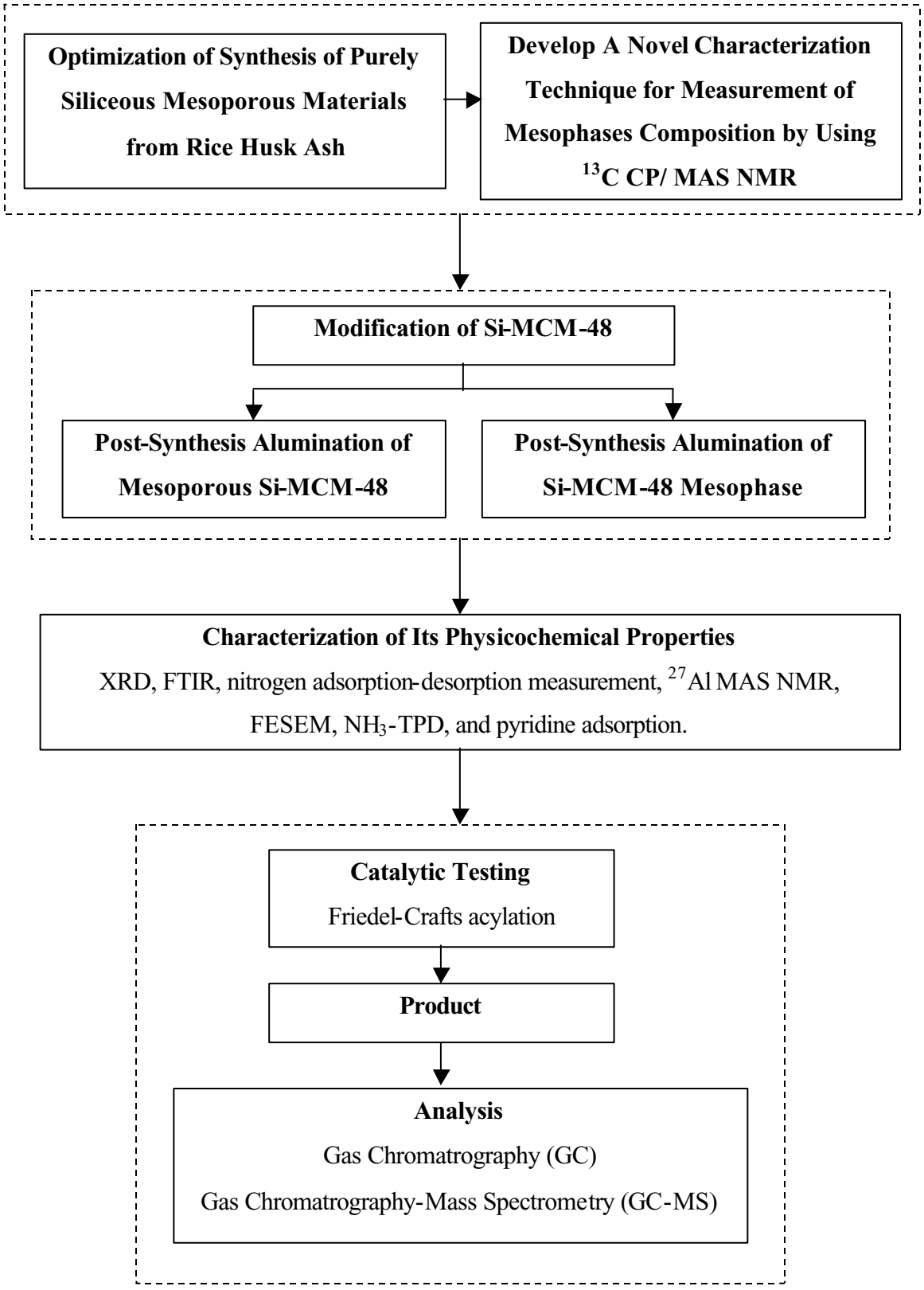

Figure 1.2 Flowchart of the research design.

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